Letters to the Editor 62-58-3-29/30 Electron Paramagnetic Resonance in the System R<sub>3</sub>Al-TiCl<sub>4</sub>

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Letters to the Editor

62-58-3-29/30

Electron Paramagnetic Resonance in the System R3Al-TiCl4

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute for Chemical Physics, AS USSR)

SUBMITTED:

January 9, 1958

Card 3/3

20-119-3-39/65

AUTHORS:

Shilov, A. Ye., Sabirova, R. D., Gorshkov, V. I.

TITLE:

On the Problem of the Formation of a Carbonium Ion in the Reactions of the Combination with Olefins (K voprosu ob obrazovanii iona karboniya v reaktsiyakh prisoyedineniya

k olefinam)

PERIODICAL:

Doklady Akademii Nauk SSSR, 1950, Vol. 119, Nr 3,

pp. 533 - 536 (USSR)

ABSTRACT:

In the first'section taking up one third of the work the authors report on previous papers, dealing with the same subject. This work investigates the absorption of ethylene in D<sub>2</sub>SO<sub>4</sub> in the case of almost complete absence of an inverse decomposition of the methylsulfuric acid. For this purpose the sition of the methylsulfuric acid. For this purpose the reaction was performed at increased pressures (about 4 atmoreaction was performed at increased pressures about 4 atmoreaction was container; one of its knees contained the -shaped glass container; one of its knees contained the deutero-sulfuric acid, in the other one the ethylene was frozen out. After this the absorption of ethylene in the sulfuric

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20-119-3-39/65

On the Problem of the Formation of a Carbonium Ion in the Reactions of the Combination with Olefins

acid began, when the container was shaken mechanically. The ethylsulfuric acid, which had formed, was hydrated with water to ethyl alcohol for the determination of its D-content, which then was transformed into ethyl chloride by a reaction with HCL in presence of zinc chloride. The ethyl chloride, which was obtained in this way, then was analyzed by the mass spectrograph MC- 1A. A table illustrates the intensity distribution of the lines in the calibration spectrum of the common ethyl chloride and in the mass spectra of the analyzed reaction products. The compositions of the formed products, which were computed from the data of this table, are composed in a second table. The only deuterium derivative, which is in the mixture in a quantity worth mentioning, is the monodeuteroethyl chloride. The production of small quantities of  $C_2H_3D_2C1$  in 2

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reactions, given here, obviously is connected with the inversability of the reaction

20-119-3-39/65

On the Problem of the Formation of a Carbonium Ion in the Reactions of the Combination with Olefins

missing. By this obviously the hypothesis of the  $\pi$ -complex experimentally is proved. From the absence of an exchange follows that in these reactions not only the reversible isothermisation of the  $\pi$ -complex into a carbonium ion is missing, but also the isomerisation of the  $\pi$ -complex into an isomeric  $\pi$ -complex. The authors thank V. L. Tal'roze for his advices in the perfomance of the mass spectrometrical analyses. There are 2 tables and 11 references, 6 of which are Soviet.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute

of Chemical Physics, AS USSR)

PRESENTED:

October 9, 1957, by N. N. Semenov, Member, Academy of

Sciences, USSR

SUBMITTED:

October 7, 1957

AVAILABLE:

Library of Congress

Card 4/4

5(4)

SOV/20-122-4-25/57

AUTHORS:

D'yachkovskiy, F. S., Bubnov, N. N., Shilov, A. Ye.

TITLE:

The Investigation of the Recombination of Triphenylmethyl Radicals by the Method of Electron Paramagnetic Resonance (Isucheniye kinetiki rekombinatsii trifenilmetil'nykh radikalov metodom elektronnogo paramagnitnogo rezonansa)

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 4, pp 629-631

(USSR)

ABSTRACT:

PERIODICAL:

According to K. Ziegler et al. (Ref 1), the inverse reaction of the recombination of triphenylmethyl radicals must proceed with an activation energy which is equal to the difference between the activation energy of the dissociation and the dissociation heat of hexaphenylethane (6 - 8 kcal). By the method of paramagnetic electron resonance, this conclusion could be confirmed by immediate measuring of the dimerization rate of triphenylmethyl radicals in the solution. A capillary with a solution of hexaphenylethane in toluene was heated to 100° and then it was rapidly cooled down to the temperature of the experiment. This operation was carried out in a thermostat which was placed within the resonator of the EPR -spectro-

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SOV/20-122-4-25/57 The Investigation of the Recorbination of Triphenylmethyl Radicals by the Method of Electron Paramagnetic Resonance

meter. In this way, noticeable superequilibrium concentrations of the triphenylmethyl radicals were obtained, and their recombination rate could be measured. The carrying out of the experiments is discussed in short. A figure shows 2 kinetic curves of the recombination of triphenylmethyl radicals at -64° and -55°. The recombination rate increases noticeably with temperature. An equation for the kinetics of the radical recombination is given, the inverse reaction is taken into account. The second diagram demonstrates the temperature dependence of the equilibrium constant and the third diagram shows the temperature dependence of the constant of the dimerization rate. The Arrhenius (Arrenius) dependence is well satisfied. Thus, the direct determination of the dimerization rate of triphenylmethyl radicals confirmed not only the existence of an activation energy of this reaction but also its value (which coincides with the difference between the activation energy of the dissociation and the energy necessary for the breaking of the C-C bond of hexaphenylethane. The authors thank T. V. Voyevodskiy (Corresponding Member, Academy of Sciences, USSR) for his interest in this paper. There are 3

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The Investigation of the Recombination of Triphenylmethyl Radicals by the Method of Electron Paramagnetic Resonance

figures and 3 references, 1 of which is Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR

(Institute of Chemical Physics, Academy of Sciences, USSR)

PRESENTED: May 23, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: May 14, 1958

Card 3/3

5(4)
AUTHORS: D'yachkovskiy, F. S., Bubnov, N. N., Shilov, A. Ye.

TITLE: Formation of Free Radicals in Bimolecular Reactions (Obrazovaniye

svobodnykh radikalov v bimolekulyarnykh reaktsiyakh)

The Reaction Between Triphenylchloromethane and Ethyl Lithium

(Reaktsiya mezhdu trifenilkhlormetanom i etillitiyem)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 5, pp870-873

(USSR)

ABSTRACT: The authors first mention some previous papers on this subject.

They investigated the interaction of triphenylchloromethane with ethyl lithium, the first act of which must be exothermic if it proceeds according to the scheme. The reaction was carried out in a thin-walled test tube which was placed in the resonator of a EPR-spectrometer. In this reaction radicals were actually observed. The hyperfine spectrum of these radicals exactly corresponds to the spectrum of absorption of triphenylmethyl radicals. A diagram shows the kinetic curves for the variation of the concentration of triphenylmethyl radicals in the course of the reaction at -44, -54, and -80°. In the first instant of the reaction, the concentration has a distinctly marked maximum and it decreases behind this maximum. The descending parts of the curve represent the recombination of the

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SOV/2o-123-5-28/5o Formation of Free Radicals in Bimolecular Reactions. The Reaction Between Triphenylchloromethane and Ethyl Lithium

triphenylmethyl radicals (formed in the first act of the reaction) before reaching the equilibrium concentration. The descending part of the curves represents the recombination of the triphenylmethyl radicals  $(2(c_6H_5)_3c_{-} \longrightarrow (c_6H_5)_3c_{-} - c(c_6H_5)_3)$  in the first act of the reaction. The experimental results prove the primary formation of the above-mentioned radicals. The maximum of the kinetic curves is not caused by an increase in temperature of the reaction mixture. The character of the kinetic curves corresponds to an accumulation of the intermediate product in the successive bimolecular reactions. The constants of velocity and the activation energy of the reaction of radical formation can be calculated from the kinetic curves found in this paper. According to these results, elementary reactions of the type R'X + YR" -> R' · + XY + · R" under suitable energy conditions proceed with the formation of free radicals of insignificant energy. It has hitherto not been possible to generalize the results of the present paper for any reaction of halogen

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SOV/20-123-5-28/50

Formation of Free Radicals in Bimolecular Reactions. The Reaction Between Triphenylchloromethane and Ethyl Lithium

alkyls with metalorganic compounds. There are 2 figures, 1  $\,$ 

table, and 12 references, 5 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR

(Institute of Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: July 16, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: July 12, 1958

Card 3/3

5(4) AUTHORS:

Shilov, A. Ye., Sabirova, R. D.

A COLUMN TO THE PROPERTY OF TH

SOV/76-33-6-30/44

TITLE:

Mechanism of the Primary Act of Thermal Ecomposition of Chlorine Derivatives of Methane (Mekhanizm pervichnogo akta termicheskogo raspada khlorproizvodnykh metana).

I. Decomposition of Carbon Tetrachloride and Methyl Chloride (I. Raspad chetyrekhkhloristogo ugleroda i khloristogo metila)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6, pp 1365-1373 (USSR)

ABSTRACT:

The thermal decomposition of methane chlorides has been insufficiently investigated; in fact, the decomposition of these compounds offers the possibility of clarifying the elementary act of the decay of molecules. In contrast to other decomposition mechanisms (radical and molecular mechanism), the above-mentioned type is termed "biradical mechanism" in the present paper.

Thermodynamic calculations show that for CH3Cl a direct splitting-off of the HCl would be more convenient than that of the Cl-atom; also

for CCl<sub>4</sub>, a scheme of decomposition has already been suggested (Ref 9);

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as, however, no precise experimental data are available on the mechanism mentioned in the title, corresponding tests were carried out in the present case. To prevent the course of secondary reactions,

Mechanism of the Primary Act of Thermal Decomposition of SOV/76-33-6-30/44 Chlorine Derivatives of Methane. I. Decomposition of Carbon Tetrachloride and

the decomposition was investigated in the gas current for a small contact time. Toluene was used as carrier gas because the latter measts with the atoms and radicals under formation of stable tenzyl radicals. The working methods, as well as a scheme of the tes, arrangement (Fig 1), are given.  $Cl_{2}$ ,  $C_{2}C_{6}$  and  $C_{2}Cl_{4}$  were determined as principal products of the thermal decomposition of CC1 with re carrier gas. The test results obtained at 6180 show (Table 1) that the reaction kinetics is of first order and the reaction proceeds in a completely homogeneous way under the given test conditions (554 - coloc). The experiments in the toluene current showed (Table 2) that the reaction-rate constant is similar to the one calculated from the tests without carrier gas. The experimental results clearly point to the reaction CCl4-ECl3+Cl3, i.e. a radical decomposition as primary act of the CCl4-decomposition, where C2Cl6 acts as intermediate product and CCl4 primarily splits off the chlorine atom. The CH3CT-decomposition was investigated at

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Mechanism of the Primary Act of Thermal Decomposition of Chlorine Derivatives of Methane. I. Decomposition of Carbon Tetrachloride and SOV/76-33-6-30/44 Methyl Chloride

843 and 874°C (toluene could not be used as carrier gas in this case), and it was ascertained that, besides HCI, mainly CH4 and C2H2 (and a little  $H'_2$ ) are generated (Tables 3,4).  $CH_3CI \rightarrow CH_3^2 + CI^*$  (17) is assumed as primary reaction, whereupon rapid exothermal reactions (18)-(23) follow. The mechanisms of the secondary reactions of the CC14- and CH3Cl-decomposition, as well as the corresponding activation energies, are indicated. There are 5 figures, 4 tables, and 18 references, 6 of which are Soviet.

ASSOCIATION:

Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva (Academy of Sciences of the USSR, Institute of Chemical Physics Moscow)

SUBMITTED:

December 3, 1957

Card 3/3

SOV/76-33-9-35/37

Shilov, A. Ye., Zefirova, A. K., Tikhomirova, N. N. 5(4)AJTHORS:

Paramagnetic Electron Resonance in the System TITLE:

 $Al(iso-C_4H_9)_3 - Ti(C_5H_5)_2Cl_2$ 

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 9, PERIODICAL:

pp 2113 - 2114 (USSR)

A. Ye. Shilov and N. N. Bubnov (Ref 1) found paramagnetic electron resonance absorption (PERA) with a g-factor of about ABSTRACT:

two in the precipitate formed by the reaction of aluminum trialkyls with titanium chlorides. The homogeneous system  $Al(iso-G_4H_9)_3$  (I) -  $Ti(G_5H_5)_2Gl_2$  (II) in toluene was investi-

gated here at room temperature. At the applied concentration

of (I) of  $2.10^{-4}$  mol/1 and ratios of (I):(II)=2:1, 10:1, 50:1 and 100:1, the authors found resonance absorption (Fig 1). The results lead to the assumption that the free electrons are

located on the atoms of Al or Ti in the system under discussion. The number of basic lines of the hyperfine structure of the (PERA)-spectrum (Fig 2) indicates that the free electron reacts

with the nucleus possessing a spin of 5/2, which would

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Paramagnetic Electron Resonance in the System Al(iso- ${}^{C_4H_9}$ )3 - Ti( ${}^{C_5H_5}$ )2 ${}^{Cl}$ 2

sov/76-33-9-35/37

correspond to the Al atom. In this connection, the free electron interacts with two protons and a hyperfine structure of the spectrum is formed due to fission on the atoms of Al and H. In conclusion, the authors thank L. I. Zakharkin and V. V. Gavrilenko for supplying substance (I). There are 2 figures and 1 Soviet reference.

SUBMITTED: February 6, 1959

Card 2/2

5.3200

80229 s/076/60/034/04/27/042 B010/B009

AUTHORS:

Shilov, A. Ye., Sabirova, R. D. (Moscow)

TITLE:

Mechanism of the Primary Act of Thermal Decomposition of Chloro-

methanes. II. Decomposition of Chloroform

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 4, pp. 860 - 865

TEXT: The kinetics of thermal decomposition of CHCl3 and CDCl3 was investigated in a continuous flow vacuum apparatus (Ref. 1). The substance to be investigated was introduced in the same manner as in earlier (Ref. 1) experiments with CCl4 and CH3Cl; the quantitative determination of the decomposition products HCl and C2Cl6 was carried out in the same way. The DCl resulting from the decomposition of CDCl3 was transformed into CH3D with CH3MgI, and determined mass spectrometrically. The CHCl decomposition was investigated in a toluene current as well as without carrier gas, at 485-599°. Surprisingly, it was found that CHCl de-

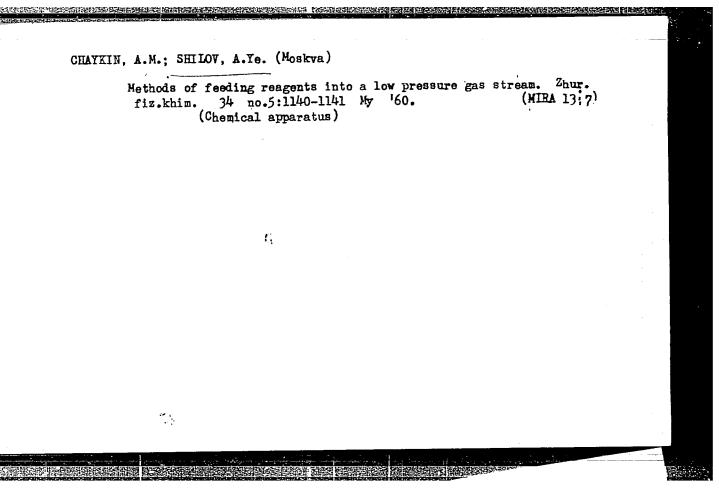
Card 1/2

Mechanism of the Primary Act of Thermal Decomposition S/076/60/034/04/27/042 of Chloromethanes. II. Decomposition of Chloroform B010/B009

composes much more readily than CCl<sub>4</sub>. The experimental results (Table 1) show that decomposition takes place practically homogeneously and according to the first order (at gas pressures above 15 torr), and that toluene does not inhibit the reaction. An addition of CCl<sub>4</sub> does not accelerate the decomposition of CHCl<sub>3</sub> (Table 2). The experiments with CDCl<sub>3</sub> (Table 3, quantities of DCl obtained at 587-652°) show that CDCl<sub>3</sub> decomposes much more slowly than CHCl<sub>3</sub> (Table 4, comparison of measured values). Contrary to Sameluk and Bernstern's assumption (Ref. 2) the primary act of the decomposition reaction is shown to be the following biradical decomposition: CHCl<sub>3</sub> —> HCl + CCl<sub>2</sub>. There are 1 figure, 4 tables, and 7 references, 3 of which are Soviet.

SUBMITTED: July 9, 1958

Card 2/2



s/020/60/132/05/30/069 BO11/B126 Zefirova, A. K., Tikhomirova, N. N., Shilov, The Structure of Some Products of the Interaction of 5.0831 Aluminum Alkyls With Derivatives of Titanium (IV) 5.3100 AUTHORS: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 5, TITLE: TEXT: The authors have extended their previously (Ref. 1) observed THAT: THE BUSHOLB HAVE EXPENDED their previously (Rel. 1) OBSERVED of Tule governing the spectra of paramagnetic electron resonance (PER) of the products of the reaction of trigian hitzlaluminum with dievelopents. the products of the reaction of tri-isobutylaluminum with dicyclopenta-PERIODICAL: dienyletitanium dichloride, to other compounds. Thus they have been able to drew some conclusions on the structure of the manufacture of the manufacture. able to draw some conclusions on the structure of the reaction products.

They are arrived the interaction of aluminum alkyla and aluminum aryla. They analyzed the interaction of aluminum alkyls and aluminum aryls: They analyzed the interaction of aluminum alkyls and aluminum as Al(Iso-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, Al(Iso-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Al(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, Al(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, Al(C<sub>3</sub>H<sub>5</sub>)<sub>3</sub>, Al(C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> (C5H5)2TiBr2, (C5H5)2TiI2. With a reagent ratio of 1: 1 in a toluenic card 1/4

81702

The Structure of Some Products of the Inter- S/020/60/132/05/30/069 action of Aluminum Alkyls With Derivatives of B011/B126
Titanium (IV)

solution, similar PER signals were received in all cases. Their g-factor was 1.975. With lower concentrations of the reagents (under 1 . 10 3 M/l), the signals have a characteristic appearance (Fig. 1), which can be explained by the presence of an undefined super-fine structure. It can be seen from the PER spectra of other Al/Ti ratios that all Al-alkyls and Al-aryls can be divided into two groups. The signals (I) (Fig. 1) for Al(CH<sub>3</sub>)<sub>3</sub>, Al(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, and AlCl(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> are not noticeably changed by a rising Al/Ti ratio. On the other hand, new signals form with the remaining Al-alkyls and -aryls, which have a well defined super-fine structure. On a change in these systems from an Al : Ti ratio of 1 : 1 to  $\sim$  20: 1, the signals I change into signals II (Fig. 2a). This latter is a doublet with a g factor of 1.985. If the ratio is increased further to ~ 50: 1, signal II is converted into signal III. Here g = 1.988 and there are eight components. In the Al-alkyls of the second group, the form of signals II and III is as independent of the nature of the alkyl as it is from the nature of the halogen atom in titanium halide. The conversion I  $\rightarrow$  III  $\rightarrow$  III led the authors to suppose that the Al-alkyls

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81702 \$/020/60/132/05/30/069 B011/B126

The Structure of Some Products of the Inter- S/O action of Aluminum Alkyls With Derivatives of BO1 Titanium (IV)

contain similar admixtures, whose quantity equates that of the titanium derivative when the Al/Ti ratio is raised, and which forms new complexes therewith. Such admixtures can be hydrides which easily form in the first group of substances analyzed, but which are totally absent in the second group. The authors tested and confirmed this hypothesis. In this second group. The authors tested and confirmed this hypothesis. In this case the doublet II can be explained by splitting on the hydrogen atom of the complex, which contains one molecule of AlH(Iso-C4H9)2° It can of the complex, which contains one molecule of some six equally in-

be seen from Fig. 3a that signal III consists of some six equally intensive lines and two lines which are three to four times less intense. Here, the super-fine structure has a natural explanation: the molecule of the reaction product contains two H atoms from two molecules of the of the reaction product contains two H atoms from two molecules of Al-hydride. Figs. 2b and 3b show the PER spectra of the products of the reaction of AlD[CH<sub>2</sub>CD(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub>. From this it foltone reaction of AlD[CH<sub>2</sub>CD(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub>.

lows that, due to the substitution of D for H, the super-fine structure completely disappears in both cases. The authors draw conclusions on the structure of the complex produced, from their results and from data in

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81702 S/020/60/132/05/30/069 The Structure of Some Products of the Interaction of Aluminum Alkyls With Derivatives of B011/B126 Titanium (IV)

the publications. They thank  $\underline{V}$ .  $\underline{V}$ .  $\underline{V}$  Voyevodskiy, Corresponding Member AS USSR for discussions, and  $\underline{O}$ .  $\underline{P}$ . Okhlobystin and  $\underline{V}$ .  $\underline{V}$ . Gavrilenko (Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds of the AS USSR)) for help in the syntheses. There are 3 figures and 4 references: 2 Soviet and 2 American.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR

(Institute of Physical Chemistry of the Academy of Sciences, USSR)

PRESENTED:

February 1, 1960, by V.N. Kondrat'yev, Academician

SUBMITTED:

January 29, 1960

Card 4/4

SHILOV, A.Ye., kand.khim.nauk

"Chemical equilibrium and rate of reactions under high pressures"
by M.G. Gonikberg. Reviewed by A.E. Shilov. Vest. AN SSSR
31 no.8:138-140 Ag '61. (MIRA 14:8)
(Chemical equilibruim)
(Gonikberg, M.G.)

89731

5.3700

1209, 1153, 1164

S/020/61/136/003/015/027 B016/B052

AUTHORS:

Zefirova, A. K. and Shilov, A. Ye.

TITLE:

Kinetics and Mechanism of the Interaction Between Aluminum

Alkyls and Titanium Halides

PERIODICAL:

Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 3,

pp. 599-602

TEXT: The authors report on the interaction mechanism and on the structure of particles taking part in the reduction process of the following compounds:  $({}^{C}_{5}{}^{H}_{5})_{2}$ TiCl<sub>2</sub> with 1) Al $({}^{C}_{2}{}^{H}_{5})_{3}$ , 2) Al $({}^{C}_{4}{}^{H}_{3})_{3}$ , and 3) Al $({}^{C}_{2}{}^{H}_{5})_{2}$ Cl (the examination of 3) was started together with E. W. Randall and L. E. Sutton in Oxford). Ad 1): in this fast reaction titanium is reduced under the formation of a light blue complex (4):  $({}^{C}_{5}{}^{H}_{5})_{2}$ TiCl<sub>2</sub> Al $({}^{C}_{2}{}^{H}_{5})_{2}$ . Ethane forms in amounts which correspond to half of the  $({}^{C}_{5}{}^{H}_{5})_{2}$ TiCl<sub>2</sub> used, thus corresponding to a disproportionation of the ethyl groups. Ethylene

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Kinetics and Mechanism of the Interaction Between Aluminum Alkyls and Titanium Halides S/020/61/136/003/015/027 B016/B052

always forms in smaller amounts than ethane. Butane is not formed. Aluminum alkyls and TiCl<sub>4</sub> show a similar reaction although titanium here is reduced to valences lower than 3+. The lower yields of ethylene are generally explained by its partial polymerization. The authors found that the products of reaction 1) yield approximately 20% of butane by the decomposition by water. They explain this by the fact that ethylene enters the Me-C bond only once during the reduction. Ad 2): titanium is slowly reduced when toluene solutions of the reagents are mixed. The light blue complex (4) does not form. The red coloring rapidly turns light blue in the presence of ethylene. Thus, methane is liberated and ethylene is absorbed. The complex of the type (4) is sublimable and has the empirical formula of  $(CH_3)_2$ AlCl· $(C_5H_5)_2$ TiCl. Propylene, butylene-1, amylene-1, other  $\alpha$ -olefins react in a similar way, and approximately equimolar amounts of ethylene are absorbed. From the formation of propane and butane during the decomposition of the reaction products by water (in the presence of ethylene), the authors conclude that the reaction takes place in accordance with the scheme of disproportionation of the alkyl groups. Here, however, the olegin first enters the Me-C bond and forms a

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Kinetics and Mechanism of the Interaction Between Aluminum Alkyls and Titanium Halides

S/020/61/136/003/015/027 B016/B052

disproportionable alkyl radical. The olefins formed during the disproportionation also enter the Me-C bond. Ad 3): the reaction follows the known scheme of Refs. 1,3 at a measurable rate. From Fig. 1 the authors conclude that the reaction proceeds according to order 1/2 until a conversion of 70-80% is reached. Then it follows the first order. On the basis of their own results and the published data, the authors regard the free radical reaction mechanism of the above reduction of titanium halide as being refuted. However, they mention a number of data supporting the ion mechanism. The scheme enclosed illustrates the reaction mechanism suggested by the authors. There are 2 figures and 8 references: 2 Soviet, 4 US, 1 British, and 1 International.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute

of Chemical Physics of the Academy of Sciences USSR)

PRESENTED:

July 3, 1960, by V. N. Kondrat'yev, Academician

SUBMITTED:

July 20, 1960

Card 3/4

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		-, 20,2	
		•	X:
· · · · · · · · · · · · · · · · · · ·	) [A1 ( $C_aH_5$ ) <sub>2</sub> CI] <sub>3</sub> $\Rightarrow$ A1 ( $C_aH_5$ ) <sub>4</sub> + A1 ( $C_aH_5$ ) <sub>2</sub> CI <sub>3</sub> ) 2 ( $C_aH_6$ ) <sub>2</sub> TiCl <sub>3</sub> + [A1 ( $C_aH_5$ ) <sub>2</sub> CI] <sub>3</sub> $\Rightarrow$ 2 ( $C_6H_6$ ) <sub>2</sub> TiCl <sub>3</sub> ·A1( $C_6H_5$ ) <sub>3</sub> TI ( $C_6H_5$ ) <sub>4</sub> TI ( $C_6H_5$ ) <sub>5</sub> CI·A1 ( $C_6H_5$ ) <sub>6</sub> CI <sub>2</sub> (111) <sup>6</sup> ) [II] $\Rightarrow$ ( $C_6H_5$ ) <sub>6</sub> TI ( $C_6H_5$ ) + A1 ( $C_6H_6$ ) CI <sub>3</sub> TI ( $C_6H_6$ ) <sub>7</sub> TC <sub>6</sub> H <sub>6</sub> + A1 ( $C_6H_6$ ) <sub>7</sub> TI ( $C_6H_6$ ) <sub>8</sub> + A1 ( $C_6H_6$ ) <sub>7</sub> TI ( $C_6H_6$ ) <sub>8</sub> + A1	ZHaliCI (II)	
3 2 2 3 3 3 3 3	) II = (C:H3) TI (C:H3) CI-AI (C:H3) CI, (III)* ) III = (C:H3) TI (C:H3 + + AI (C:H3) CI, (III)* ) (C:H3TICH++ AI (C:H3 CI) TI (C:H3 CI)	VO.11.0	
3	$I(C_5 \cap s)_2 \cap I(C_4 \cap s)_2 + AI(C_2 \cap s)_2 \rightarrow (C_5 \cap s)_3 \cap I(C_4 \cap s)_3 + AI$	$(C_2H_5)_3$	
5 6	) $(C_5H_5)_2$ Ti $(C_2H_5)_2 \rightarrow (C_5H_5)_3$ Ti $+$ $C_2H_6 + C_4H_4$ ) $(C_2H_2)_2$ Ti $+$ II $\rightarrow$ $(C_5H_5)_2$ TiCl $+$ $(C_2H_5)_2$ Ti Cl <sub>2</sub> Al $(C_2H_5)_2$		
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			(D) report and the control of the co
Card 4/4			Chicago Carlo

5/190/62/004/011/007/014 B106/B101

AUTHORS:

Shilov, A. Ye., Shilova, A. K., Bobkov, B. N.

TITLE:

Reaction of  $\alpha$ -olefins with soluble complex Ziegler catalysts

and the mechanism of polymerization initiation

PERIODICAL:

Vysokomolekulyarnyye soyedineniya, v. 4, no. 11, 1962,

TEXT: In a previous paper (Ref. 3: A. K. Zefirova, A. Ye. Shilov, Dokl. AN SSSR, 136, 599, 1961) the hypothesis was put forward that the polymerization of ethylene is initiated by an ionic mechanism in the presence of a Ziegler catalyst obtained by bringing dicyclopentadienyl titanium into reaction with aluminum alkyls. This hypothesis was studied experimentally on the basis of the catalytic system  $(C_5H_5)_2TiCl_2-Al(CH_3)_2Cl$ .

. Since the polymerization of ethylene coincides with the reduction of Ti4+ to Ti3+, which is accompanied by a change in color, the process was studied by spectrophotometry. Titanium is reduced by reaction of  $(c_5H_5)_2$  TiCl  $_2$  with Al(CH $_3$ ) Cl only in the presence of  $\alpha$ -olefins (studied in

Card 1/3

Reaction of  $\alpha$ -olefins...

S/190/62/004/011/007/014 B106/B101

ethyl groups can start without preliminary incorporation of the olefin. A rough estimate of the ion concentration in the reaction studied (using benzene as a solvent) with the aid of the Walden equation yielded  $5.10^{-9}$  mole/l for medium concentrations of complex A of  $\sim 5.10^{-3}$  mole/l. Hence, the concentration of ions is very low and their reactivity very high. There are 5 figures. The most important English-language references are: W. P. Long, D. S. Breslow, J. Amer. Chem. Soc., 82, 1953, 1960; A. N. Maki, E. W. Randall, J. Amer. Chem. Soc., 82, 4109, 1960; G. Wilkinson, J. M. Birmingham, J. Amer. Chem. Soc., 76, 4281, 1954.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical

SUBMITTED:

June 30, 1961

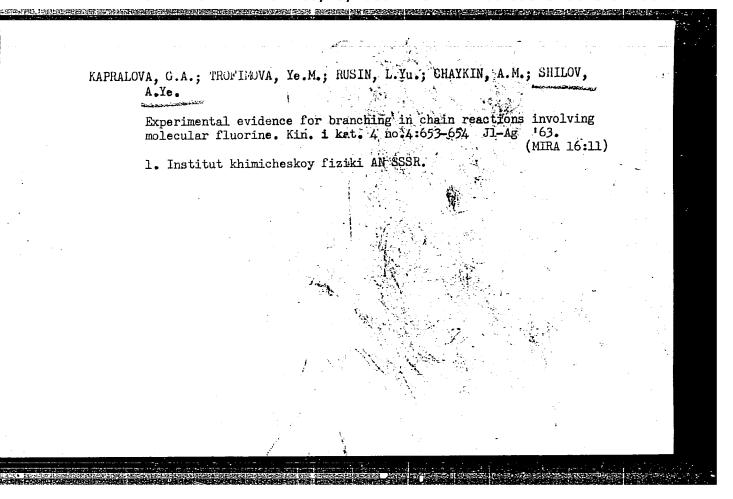
Card 3/3

VEDENEYEV, V.I.; CHAYKIN, A.M.; SHILOV, A.Ye.

Branching in chain reactions involving molecular fluorine. Kin.i kat. 4 no.2:320-321 Mr-Ap 163. (MIRA 16:5)

1. Institut khimicheskoy fiziki AN SSSR. (Fluorine) (Hydrogen) (Fluorine organic compounds)

"Chemical kinetics and catalysis" by G.M.Panchenkov,
V.P.Lebedeva. Reviewed by N.S.Enikolopian, A.E.Shikov.
Kin.i kat. 4 no.2:322-325 Mr-Ap '63. (MIRA 16:5)
(Chemical reaktion, Rate of)(Catalysis)
(Panchenkov, G.M.) (Lebedev, V.P.)



D'YACHKOVSKIY, F.S.; SHILOV, A.Ye.

Effect of the nature of halogen on the rate of reaction between ethyllithium and alkyl halides. Kin. i kat. 4 no.6: 919-923 N-D '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

D'YACHKOVSKIY, F.S.; SHILOV, A.Ye.

THE PROPERTY OF THE PROPERTY O

Reaction of the mechanism of ethyllithium with ethyl iodine. Zhur.ob.khim. 33 no.2:406-411 F '63. (MIRA 16:2)

1. Institut khimicheskoy fiziki AN SSSR. (Lithium) (Ethane)

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s/020/63/148/001/026/032
                                                                                                                                                                                                                                                                                             B101/B186
                                                                                    Stepovik, L. P., Shilova, A. K., Shilov, A. Ye.
                                                                                       Kinetics and mechanism of the initiation of ethylene
                                                                                        polymerization on a soluble Ziegler-type complex catalyst
                                                                                             Akademiya nauk SSSR. Doklady, v. 148, no. 1, 1963, 122-125
AUTIORS:
        TEXT: In a previous paper (Vysokomolek. soyed., 4, no.11 (1962)) the following reaction pattern was found for the polymerization of olefins on a (m-C-H-)-TiCl- + Al(CH-)-Cl catalyst:
   TITLE:
        PERIODICAL:
                 (C_5H_5)_2^{\text{TiCl}_2} + \text{Al}(CH_3)_2^{\text{Cl}} \rightarrow (C_5H_5)_2^{\text{Ti}(CH_3)}^{\text{Cl}} \rightarrow (C_5H_5)_2^{\text{Cl}} \rightarrow (C_5H_5)_2^{\text{Ti}(CH_3)}^{\text{Cl}} \rightarrow (C_5H_5)_2^{\text{Cl}} \rightarrow 
             on a (\pi^{-C}5^{H}5)^{2} TiCl<sub>2</sub> + Al(CH<sub>3</sub>)<sub>2</sub>Cl catalyst:
                   A \rightleftharpoons (C_5^{H_5})_2^{Z_{1CH_3}^{+}} + A1(GH_3)^{Cl_3}; (C_5^{H_5})_2^{T_1CH_3} + RCH = CH_2
                     \rightarrow (c_{5}^{H_{5}})_{2}^{TiCH_{2}CH(R)CH_{3}^{+}}; (c_{5}^{H_{5}})_{2}^{TiCH_{2}CH(R)CH_{3}^{+}} + AlcH_{3}^{Cl_{3}^{-}}
                         \longrightarrow ({}^{C_5}{}^{H_5})_2{}^{\text{TiCH}}_2{}^{\text{CH}}(R){}^{\text{CH}}_3{}^{\text{Cl}} \cdot \text{Al}({}^{\text{CH}}_3){}^{\text{Cl}}_2 \text{ (complex B)};
                             (c_{5}^{H}_{5})_{2}^{TiCH_{2}CH(R)CH_{3}Cl \cdot Al(CH_{3})Cl_{2}} \rightarrow (c_{5}^{H}_{5})_{2}^{TiCl \cdot AlCH_{3}Cl_{2}} (complex C).
                                  Card 1/3
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S/020/63/148/001/026/032 B101/B186

Kinetics and mechanism of the ...

The reduced titanium in complex C is no longer active. In the present paper a direct proof of this order of reaction for ethylene is given, based on determining spectroscopically the variations in concentration of the complexes A, B (in the present case R=H) and C from the variations in optical density of the solution at 660 and 610 m $\mu$  for A and B, and at 720 and 520 m $\mu$  for C. The determination of the concentration of C on the basis of the e.p.r. spectrum agreed well with optical data. It was found that the sum A+B+C remained constant and that the reaction occurred in the order A  $\longrightarrow$  B  $\longrightarrow$  C. This is the first direct proof that the olefin molecule is added to the Ti-C bond. The kinetic equation for complex B is:  $(d[B]/dt)_0 = k[A]^{1/2}[C_2H_4]$ . The following data were found by experiments:  $k_{22} c_{10}^{-10^3}$ ,  $1^{1/2} \cdot mole^{-1/2} \cdot sec^{-1}$  equaled 4.9±0.2 for  $C_2H_4$ , 1.7±0.1 for  $c_3^{H_6}$ , 0.51±0.04 for  $c_7^{H_{14}}$ , and 0.037 for  $c_2^{H_3}$ Cl. The specific effect which the catalyst investigated exerts on the ethylene polymerization is explained by the fact that in this case the linear C3H7 radical is formed from  $C_2H_4$ , whereas the branched group  $-CH_2-CH(CH_3)R$  is formed from the Card 2/3

Kinetics and mechanism of the ...

S/020/63/148/001/026/032 B101/B186

 $\alpha$ -olefins of the formula RCH=CH $_2$ ; this group is easily converted to the isoolefin  $CH_2=c(CH_3)R$ , with the titanium being reduced and termination occurring. This generally holds for Ziegler catalysts by which ethylene, but no other  $\alpha$ -olefins, can be polymerized. An active B complex is formed only with  $C_2H_4$ . The ratio  $k_2/k_1$  between the constant  $k_2$  for chain propagation and k1 for initiation was found to be 18.9, in good agreement with the value, 19, found from the ratio between maximum rate of polymerization at constant  $p_{C_2H_4}$  and the initial rate of complex formation. These results do not confirm the assumptions made by J.S.W. Chien (J.Am. Chem. Soc., 81, 86 (1959)) and G.L. Karapinka, W.L. Carrick (J. Polym. Sci., 55, 145 (1961)). There are 3 figures and 1 table.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

PRESENTED:

July 23, 1962, by N.N. Semenov, Academician

SUBMITTED:

July 23, 1962

Card 3/3

L 12587-63 EPR/EWP(j)/EPF(c)/EWP(q)/EWT(m)/BDS AFFTC/ASD Ps-4/Pc-4/ACCESSION NR: AP3003225 S/0020/63/150/006/1282/1284,

AUTHOR: Kapralova, G. A.; Rusin, L. Yu.; Chaykin, A. M.; Shilov, A. Ye.

TITLE: Elemental reactions of molecular fluorine

SOURCE: AN SSSR. Doklady, v. 150, no. 6, 1963, 1282-1284

TOPIC TAGS: molecular fluorine, fluorine, hydrogen, carbon, frozen olefin, ethylene, divinyl, hydrogen iodide, luminescence, flame diffusion, methane

ABSTRACT: The great reactive capacity of molecular fluorine, as compared to other halogens, is explained by its affinity for H, C, and metals, and the high energy of its bonding with C, H, and Me (over 100 kcal/mol) accounts for certain features of the reactions illustrated here, some of which involve the release of enormous amounts of energy and may lead to chain reactions. The authors give the results of their studies on the kinetics and mechanism of the 2 types of elemental reaction shown in equations (1) and (2) of the Enclosure. At liquid N sub 2 temperatures, type (2) reactions occur with the formation of free radicals by gaseous F sub 2 on interaction with frozen olefins. Measured with a thermocouple vacuum gage to determine the fall of F sub 2 pressure, the reaction was too fast for measurement when ethylene and divinyl were used. With chloro-substituted ethylene, the

L 12587-63 ACCESSION NR: AP3003225

reaction rate decreased. In detailed kinetic studies on trichloroethylene bound to F sub 2, measurements of the surface size of the frozen olefin by the BET method showed that the quantity of F sub 2 molecules taken up by the olefin at -196C was almost identical to the number of olefin molecules at the surface; deeper layers reacted only when the temperature was increased. The energy of the reaction of C sub 2 HCl sub 3 was ca. 0.5 kcal/mol over the temperature range -196C to -163C; thus for olefins with a smaller number of Cl atoms in the molecule, especially ethylene, the energy of activation must be practically nil. Flamediffusion measurements of the reaction rate of molecular F sub 2 with gaseous ethylene by Kistyakovskiy's method were made to study the reactions shown in equations (3), (4), (5), (6) of the Enclosure. Although the energy of activation was quite low, it was decidedly higher than in the surface reaction of F sub 2 with olefins. The reaction of F sub 2 with hydrogen iodide was accompanied by distinct luminescence, the spectrum corresponding to the known spectrum of excited FI\* molecules. With an excess of HI, the stable reaction products were molecular iodine and hydrogen fluoride. Flame diffusion determination of the velocity constants in experiments in which F sub 2 was added via a nozzle to a stream of HI was compared with initial flame-diffusion heating under different flow conditions. The good correspondence indicates that rate of luminescence and heat emission are functions of the same process. Flame-diffusion studies showed little reaction

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L 12587-63 ACCESSION NR: AP3003225

between F sub 2 and CH sub 4 or HCl under comparable conditions and these reactions were practically thermo-neutral, in contrast to the markedly exothermic reactions of F sub 2 with olefins and HL. These findings further confirm the close relationship between activation energy and thermal effect, which is evidently analogous to Polyani's law for radical reactions. The paper was presented by Academician N. N. Semenov on 21 Feb 1963. Orig. art. has: 2 figures and 6

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, Academy of Sciences SSSR)

SUBMITTED: 00

DATE ACQ: 24Jul63

ENCL: 01

SUB CODE: CH

NO REF SOV: 003

OTHER: 007

Card 3/43

ABAKUMOV, G.A.; SHILOV, A.Ye.; SHULYNDIN, S.V.

Electron paramagnetic resonance of the products of interaction between dicyclopentadienyl vanadium dichloride and aluminum alkyls. Kin. i kat. 5 no.2:228-234 Mr-Ap 164.

(MIRA 17:8)

1. Institut khimicheskoy fiziki AN SSSR.

DZHABIYEV, T.S.; SABIROVA, R.D.; SHILOV, A.Ye.

Mechanism of interaction between triethylaluminum and tetrabutyl titanate, and the structure of complexes formed. Kin. i kat. 5 no.3:441-445 My-Je '64. (MIRA 17:11)

1. Institut khimicheskoy fiziki AN SSSR.

while, LaIne; CHAYKIN, A.M.; SELLAY, A.Ye.

Thetron paramagnetic resonance spectra of halogen atoms in gasphase branched chain reactions. Kie, i kat. 5 no.6:1121-1123 N-D 164. (MIRA 18:3)

THE RESIDENCE OF THE PROPERTY OF THE PROPERTY

1. Institut khimicheskoy fiziki AN SSSR.

SEMENOV, N.N.; SHILOV, A.Ye.

Part played by excited particles in branched chain reactions. Kin. i kat. 6 no.1:3-16 Ja-F '65.

(MIRA 18:6)

1. Institut khimicheskoy fiziki AN SSSR.

GRIGORYAN, E.A.; D'YACHKOVSKIY, F.S.; SHILOV, A.Ye.

Polymerization of deuteroethylene on the homogeneous catalytic system (C5H5)<sub>2</sub>TiCl<sub>2</sub> + Al(CH<sub>3</sub>)<sub>2</sub>Cl. Vysokom.soed. 7 no.1:145-149
Ja '65. (MIRA 18:5)

1. Institut khimicheskoy fiziki AN SSSR.

MECHIFOREMAN, G.N.: Deskina, G.M.: CHILOVA, E.K.: SHILOV, A.Ye.

M. Chanion of mitrogen fizetion in the realting system
[John] 1001 - J.E.MgBr. Dalvi. AN OBER 124 massi 562-1063
0 165.

(MIRA 16:10)
1. Institute Milian sheekey fluited AN BESS. Submitted Moren 22, 1965.

DZHABIYEV, T.S.; SHILOV, A.Ye.

CONTROL HANGE CONTROL SANGER BUTCH CONTROL CON

Electron paramagentic resonance and structure of Ti (III) complexes formed during the reduction of cyclopentadiene compounds of Ti (IV) by alkyl derivatives of aluminum. Zhur. strukt. khim. 6 no.2:302-303 Mr-Ap '65. (MIRA 18:7)

1. Filial Instituta khimicheskoy fiziki AN SSSR, Noginsk.

ACC NR: AP600216	4 SOURCE COI	(c) IJP(c) JD/WW/JW/JWD DE: UR/0195/65/006/006	/0977/0981
AUTHOR: Kapralo		Ye. H.; Shilov, A. Ye	63
ORG: Institute ( Fiziki AN SSSR)	of Chemical Physics, A	AN SSSR (Institut khimi	cheskoy
TITLE: The upper	r ignition limit in t	the reaction of fluorin	e with
OURCE: Kinetika	ı i kataliz, v. 6, no	6, 1965, 977-981	
TOPIC TAGS: flan	ae, combustion, propu	Ision, ignition limit	
his reaction, bu	. Had been assumed th	ith fluorine is often at no branching took p xplosion. A mechanism t in principle from a	lace in
	0) H <sub>3</sub> + F <sub>3</sub> → F + HF + H 1) F + H <sub>3</sub> → HF + H 2) H + F <sub>3</sub> → HF* + F 3) HF* + F <sub>3</sub> → HF + 2F 4) HF* + M → HF + M	5) H+O <sub>2</sub> +M→HO <sub>2</sub> +M 5') F+O <sub>4</sub> +M→FO <sub>2</sub> +M 6) F+wall>termination 6') H+wall>termination	

#### L 11112-66

ACC NR: AP6002164

The experimental results obtained in this work clearly indicate the existence of an upper pressure limit. Above the limit the reaction is slow, below the limit an explosion occurs. Branching of the chain reaction taking place above the limit is attributed to excited HF molecules. The reaction of an excited HF molecule with a fluorine molecule probably involves a chemical reaction of the type:

。 1. 10.10元子,

 $F-F+H^{\bullet}-F\rightarrow F+HF+F$ 

rather than simple energy transfer by collision, which is extremely improbable. The authors intend to investigate the reaction mechanism in more detail and to refine the value of  $k_3/k_4$ . Orig. art. has: 6 figures and 1 table. [VS]

SUB CODE: 21/ SUBM DATE: 14Jul64/ ORIG REF: 003/ OTH REF: 004

80

Card 2/2

SHILOV, B.M.; KARMANOV, V.V.: BAGRAMOV, E.S.; YEVSEYEVA, A.M.; LUKOMSKIY, I.K.; ROTOVA, M.N.; BELOVA, L.G.; MARTYNOV, V.I.; obshchiy red.; SHILOV, P.D., red.; VENGERSKAYA, S.R., tekhn.red.

[Economy of Daghestan A.S.S.R.; statistical collection] Narodnoe khoziaistvo Dagestanskoi ASSR; statisticheskii sbornik. Makhachkala, Dagstatizdat, 1958. 119 p. (MIRA 12:12)

1. Daghestan A.S.S.R. Statisticheskoye upravleniye. 2. Statisticheskoye upravleniye Dagestanskoy ASSR (for B.M.Shilov, Karmanov, Bagramov, Yevseyeva, Lukomskiy, Rotova, Belova). 3. Nachal'nik Statisticheskogo upravleniya Dagestanskoy ASSR (for Martynov).

(Daghestan-Statistics)

MARTYNOV, V.I.; SHILOV, B.M.; KARMANOV, V.V.; YEVSEYEVA, A.M.; LUKOMSKIY, I.K.; MIKHAYLOVA, T.N.; CHEKMAREVA, M.M.; VENGERSKAYA, S., tekhn.red.

[Soviet Daghestan in 40 years; statistical collection] Sovetskii Dagestan za 40 let; statisticheskii sbornik. Makhachkala, Gosstatizdat, 1960. 157 p. (MIRA 13:8)

1. Daghestan A.S.S.R. Statisticheskoye upravleniye. 2. Nachal'nik Statisticheskogo Upravleniya Degestanskoy ASSR (for Martynov). (Daghestan--Statistics)

AUTHOR: Zvara, I.; Chuburkov, Yu. T.; Tsaletka, R.; Zvarova, T. S.; Shalayevskiy, M. R.; Shilov, B. V.  ORG: none  TITLE: Chemical properties of the element 104, V  SOURCE: Atomnaya energiya, v. 21, no. 2, 1966, 83-84  TOPIC TACS: element NA, transuranium element, chemical property, nuclear reaction, fission product, isotope separation  ABSTRACT: Chemical identification of the new element 104 has been attempted in a comparative study of the curium, californium, hafnium and new element chlorides. Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by physical means of the III B and earlier developed, of a rapid, continuous separation of the elements of the III B and earlier developed, of a rapid, continuous separation of the elements of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements of the Joint Institute for Nuclear Research. Radioactive isotopes proaccelerator of the Joint Institute for Nuclear Research. Radioactive isotopes produced were chlorinated by a mixture of NbCl <sub>5</sub> and ZrCl <sub>4</sub> vapors in the 220—350C range duced were chlorinated by a mixture of NbCl <sub>5</sub> and ZrCl <sub>4</sub> vapors in the 220—350C range in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron.	I. 13031-56 EWT(m)/EWP(t)/ETT 1JP(c) 3D  SOURCE CODE: UR/0089/66/021/002/0083/0084  ACG NR: AP6029794	/ :
SOURCE: Atomnaya energiya, v. 21, no. 2, 1966, 83-84  TOPIC TAGS: element 34, transuranium element, chemical property, nuclear reaction, fission product, isotope separation  ABSTRACT: Chemical identification of the new element 104 has been attempted in a comparative study of the curium, californium, hafnium and new element chlorides. Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by an authors applied their own method, et al. Atomnaya energiya, 17, 310, 1964]. The authors applied their own method, earlier developed, of a rapid, continuous separation of the elements of the III B and earlier developed, of a rapid, continuous separation of the elements of the elements. IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 duced were chlorinated by a mixture of NbCl <sub>5</sub> and ZrCl <sub>4</sub> vapors in the 220-350C range in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron the walls of the chamber and in the special filters, while	AUTHOR: Zvara, I.; Chuburkov, Yu. T.; Tsaletka, R.; Zvarova, T. S.; Shalayevskiy, M. R.; Shilov, B. V.	!
TOPIC TAGS: element 104, transuranium element, chemical property, nuclear reaction, fission product, isotope separation  ABSTRACT: Chemical identification of the new element 104 has been attempted in a comparative study of the curium, californium, hafnium and new element chlorides. Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by physical means of the III B and earlier developed, of a rapid, continuous separation of the elements of the III B and earlier developed, of a rapid, continuous separation of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements accelerator of the Joint Institute for Nuclear Research. Radioactive isotopes produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>23</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>24</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>25</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target	ORG: none	
TOPIC TAGS: element 104, transuranium element, chemical property, nuclear reaction, fission product, isotope separation  ABSTRACT: Chemical identification of the new element 104 has been attempted in a comparative study of the curium, californium, hafnium and new element chlorides. Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by physical means only [G. N. Flerov Previously, the 104260 isotope was identified by physical means of the III B and earlier developed, of a rapid, continuous separation of the elements of the III B and earlier developed, of a rapid, continuous separation of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements accelerator of the Joint Institute for Nuclear Research. Radioactive isotopes produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>23</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>24</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>25</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target	TITLE: Chemical properties of the element $104$	
ABSTRACT: Chemical identification of the new element 104 has been attempted in a comparative study of the curium, californium, hafnium and new element chlorides. Previously, the 104260 isotope was identified by physical means only [G. N. Flerov et al. Atomnaya energiya, 17, 510, 1964]. The authors applied their own method, earlier developed, of a rapid, continuous separation of the elements of the III B and earlier developed, of a rapid, continuous separation of the elements of the Periodic Table to a mixture of gaseous chlorides of the elements IV B groups of the Periodic Table to a mixture of gaseous chlorides of the elements produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 produced by nuclear reactions. A PuO <sub>2</sub> target was bombarded with Ne <sup>22</sup> ions in a Y-300 accelerator of the Joint Institute for Nuclear Research, Radioactive isotopes produced were chlorinated by a mixture of NbCl <sub>5</sub> and ZrCl <sub>4</sub> vapors in the 220—350C range in the chamber of the cyclotron. The curium, californium, and scandium isotope in the chamber of the cyclotron. The curium, californium, and scandium isotope chlorides were adsorbed on the walls of the chamber and in the special filters, while	COURCE: Atomnava energiya, v. 21, no. 2, 1966, 83-84	·
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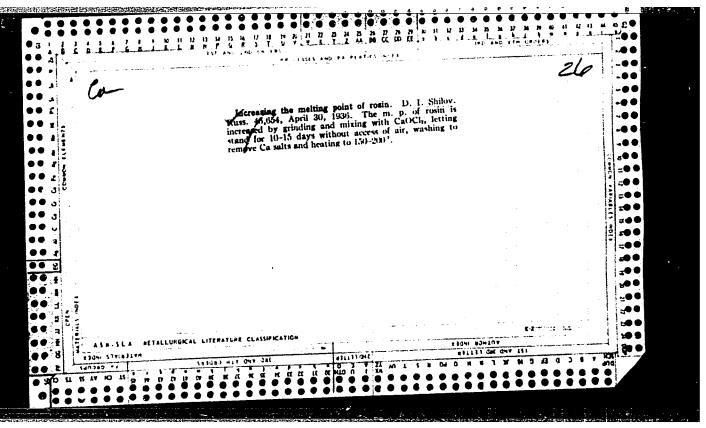
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Zr., Hf and  $104^{260}$  isotopes were transported in a stream of nitrogen to a fission event detector. The presence of the  $104^{260}$  isotope was recorded by the detector in the gaseous stream transporting the IV B group element chlorides. A total of 12 atoms of the  $104^{260}$  isotope was recorded during a series of experiments. Recurrence intervals of all 12 spontaneous fission events confirmed the earlier established half-life of the new element  $(0.3 \pm 0.1 \text{ sec})$ . Thus, confirmation was obtained of the earlier advanced hypothesis of a sharp difference in the chemical property between the 104 element and transuranium elements which were discovered in the past few years. The atomic number of the new element was determined and the element 104 was shown to be close to hafnium, hence to belong to the IV b group of the Periodic Table of the Elements. Thanks are expressed to G. N. Flerov, Corresponding Member of the Academy of Sciences SSSR.

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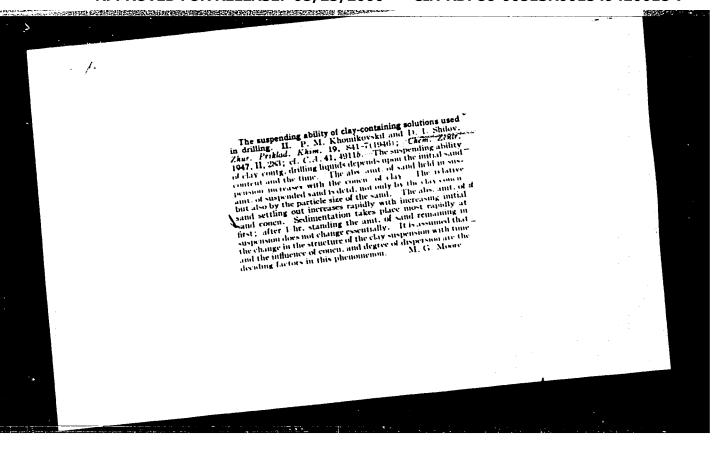
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SHILOV, D. 1.

PA 18T12

USSR/Petroleum Industry Lime

Aug 1947

"Preparation of Lime Solution by Tsurinov's and Kvirikashvil's Methods," D. I. Shilov, 5 pp

"Neftyanoye Khozyaystvo" Vol XXV, No 8

This method was used at the Tuymazaneft' industry. Tables with results and observations. New method of preparing lime solutions by means of rollers and grinders has better quality solutions than old method. New method is more economical, as less lime has to be used. Also, is more efficient in lining the walls of the bore.

18T12

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1. Zlatoustskiy zavod metallokonstruktsiy (for Khar'kov).

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mostov.

ARZYMBETOV, S.; AMANZHOLOV, S., professor, redaktor; NURUSHEV, M., redaktor; SHILOV, F.G., redaktor; ZLOBIN, M.V., tekhnicheskiy redaktor

[Russian-Kazakh agricultural dictionary with the principal biological terms] Russko-kazakhskii sel'skokhoziaistvennyi slovar'; s osnovnymi terminami biologii. Izd. 2-oe, perer. i dop. Alma-Ata, Kazakhskoe gos. izd-vo. 1955. 270 p. (MLRA 9:8)

(Russian language--Dictionaries--Kazakh)
(Agriculture--Dictionaries)

SEMENYUK, Ivan; KULAKOV, N., redaktor; SHILOV, F., redaktor; OYSTRAKH, V., tekhnicheskiy redaktor

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1. Brigadir prokhodchikov shakhty No. 37 kombinata "Karagandaugol!" (for Semenyuk)

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KALIYEV, Botay; KULAKOV, N., redaktor; SHILOV, F., redaktor; OYSTRAKH, V., tekhnicheskikh redaktor

[Safety engineering under public control] Teknniku bezopasnosti - pod obshchestvennyi kontrol. Alma-Ata. Kazakhskoe gos. izd-vo, 1956. 11 p. (HIRA 9:10)

PIL'NEN'KIY, Yevgeniy Ivanovich; SHILOV. F., red.; KOZLOV, S., tekhn. red.

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(Scaffolding) (MIRA 11:7)

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LYUBOSHCHINSKIY, Dmitriy Markovich; VAL'SHTEYN, G., redaktor; SHILOV, F., redaktor; OYSTRAKH, V., tekhnicheskiy redaktor

CHEROLOGICA CHEROLOGICA DE COMPANION CONTROLOGICA CONTROLOGICA CONTROLOGICA DE CONTROLOGICA DE CONTROLOGICA CO

[Give coupled cutter-loaders a clear track ahead; the work practice of V.Borodin's rapair crew at the S.M.Kirov Mine] Sdvoennym kombainam - shirokuiu dorogu; iz opyta raboty remontno-podgotovitel'noi brigady shakhty im. S.M.Kirova V.Borodina. Alma-Ata, Kazakhskoe gos. izd-vo, 1956. 13 p.

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NUDEL'MAN, Sergey Borisovich; SHILOV, F.G., redaktor; BARAG, T.Ya., redaktor; CHEZHIK, F., tekhnicheskly redaktor

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PIL'NEN'KIY, Yevgeniy Ivanovich; SHILOV, F.G., redaktor; KOZLOV, S.V., tekhnicheskiy redaktor

[Building with reinforced concrete openwork girders and pressed reed slabs] Stroitel'stvo iz azhurnogo zhelezobetona i kamyshito-vykh plit. Alma-Ata, Kazakhskoe gos. izd-vo, 1956. 25 p. (MLRA 9:10) (Building)

KURDYAYAY, Boris Sergeyevich; SHILOV, F.G. redaktor; BARAG, T.Ya, redaktor; KOZLOV, S.V., tekhnicheskiy redaktor

[Engineer G.A.Maniukov's system of bricklaying] Kirpichnaia kladka sistemy inzhenera G.A.Maniukova. Alma-Ata, Kazakhskoe gos. izd-vo, 1956. 26 p. (MIRA 9:10) (Building blocks) (Bricklaying)

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SHILOV, F.G., redaktor; KIRPICHNIKOV, V.A., redaktor; ZLOBIN, M.V., tekhnicheskiy redaktor

[Karaganda's coal is for the motherland; a collection of articles by coal miners of the Karaganda Basin] Ugol' Karagandy - rodine; sbornik statei ugol'shchikov i shakhtostroitelei Karagandinskogo ugol'nogo basseina. Alma-Ata, Kazakhskoe gos. izd-vo 1956. 56 p.

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BRAND, Vladimir Eduardovich; RATURINSKIY, Yevgeniy Petrovich; KULIKOVSKAYA, Nadezhda Borisovna; SHILOV, F.G., redaktor; OYSTRAKH, V.G., tekhnicheskiy redaktor

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gos.izd-vo. 1957. 134 p. (MLRA 10:9)
(Kazakhstan--Industries) (Kazakhstan--Building)

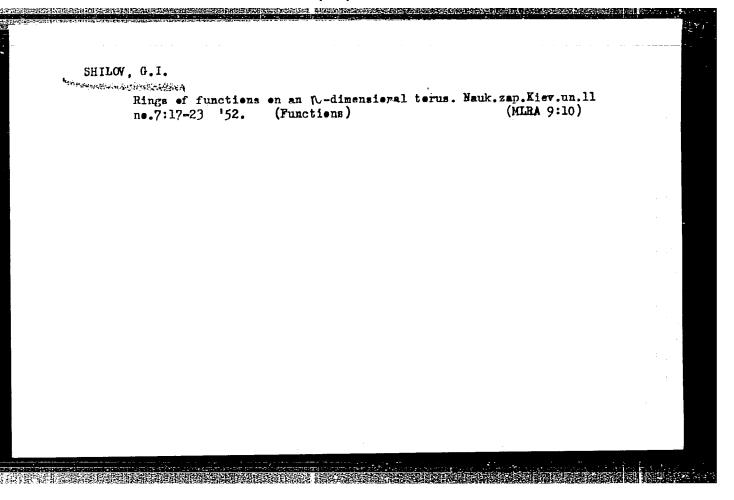
PALIGOV, Nikolay Nikitich; SHIIOV, F.G., red., ZLOBIN, M.V., tekhn. red.

[Altering Kazakhstan's nature; popular science sketch]
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ocherk. Alma-Ata, Kazakhskoe gos.izd-vo, 1955. 39 p.
(MIRA 16:8)

1. Deystvitel'nyy chlen AN Kaz.SSR (for Pal'gov). (Kazakhstan--Economic geography)

- LIVANOV, Mikhail Mikhaylovich; BELIKOV, Ye.F., dotsent, retsenzent; SHILOV, F.Ye., inzhener-geodezist, retsenzent; LETOVAL'TSEV, I.G., dotsent, red.; VASIL'YEVA, V.I., red.izd-va; ROMANOVA, V.V., tekhn. red.;

[Surveying in construction] Geodeziia v stroitel'stve. Moskva, Gosgeoltekhizdat, 1963. 312 p. (MIRA 16:6) (Surveying)



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The TPO-1 instrument for checking the thickness of nonmagnetic coatings and the investigation of the performance of some elements of this device. Izv.vys.ucheb.zav.; prib. no.4:46-56 (MIRA 13:5)

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 Rekomendovana kafedroy tekhnologii priborostroyeniya.
 (Thickness measurement)

SHILOV, German Ivanovich; VALITOV, Abdrashid Mukhamed-Zakirovich; GUTKIN, V.G., red.

[New devices for the control of the thickness of metallic and nonmetallic coatings] Kovye pribory dlia kontrolia tolshchiny metallicheskikh i nemetallicheskikh pokrytii. Leningrad, 1964. 30 p. (MIRA 17:11)

VALITOV, A. M-Z.; SHILOV, G.I.

The TPO-V device for precision checks of coating thickness. Izm.tekh. no.6:14-17 Je 164. (MIRA 17:12)

KLIMENKO, N.N. (Vladivostok); SHILOV, G.K. (Vladivostok)

Building multiple-story houses on weak soils. Osn., fund. i mekh.
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SHILOV, G. M.

At the Dneproretrovsk-Mining Institute in Artem Sergeyev from April 1939 to April 1947, the following dissertations were defended in connection with attaining the scholarly degree of Candidate of Technical Sciences (specializing in mining electrical engineering: G. M. Shilov on 27 March 1941 defended his dissertation on the subject "Traveling electrooptical signaling in electric-locomotive hauling in the iron mines of the Krivoy Rog Basin".

The official opponents of this dissertation were Candidate of Technical Sciences  $\Lambda$ . I. Selishchev and Candidate of Technical Sciences Docent S. A. Volotkovskiy.

An analysis was made of the elementary relay-contact systems of signaling in electric-locomotive hauling. A model was constructed and a typical system of electric signaling was worked out for the Krivoy Rog iron mines. A theoretical and experimental investigation of setting relays was presented.

SO: Elektrichestvo / Electricity /, No. 10, October 1947. Moscow.

STEPANOVA, Z.S., kand.khim.nauk; SHIIOV, G.M., inzh.

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Enthematics - Function Theory

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"Trudy Matematicheskogo Instituta imeni V. A.

Steklova" Vol XII

An investigation of the "normierte Ringe" of I. Galfand as they pertain to various infinite series,
Fourier's series, complex functions, and convergence and divergence in integrals.

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SHILOV, G. Ye

contains  $D_n$ , then it contains  $\tilde{C}_P$  for some  $\tilde{P}$ . Previously published results [Gel'fand, Ralkov, and Silov, paper reviewed above; Silov, Trav. Inst. Math. Stekloff 21 (1947); these Rev. 9, 596] permit comparison of R with normed Silov, G. E. On a property of rings of functions. Doklady rings built by introducing in D<sub>o</sub> norms defined by the expressions

 $\max_{a \le 1 \le n} \sum_{n=0}^{\infty} |x^{(n)}(t)|^n \alpha_n |n|^n$ 

derivatives there. The following theorem is proved: if R

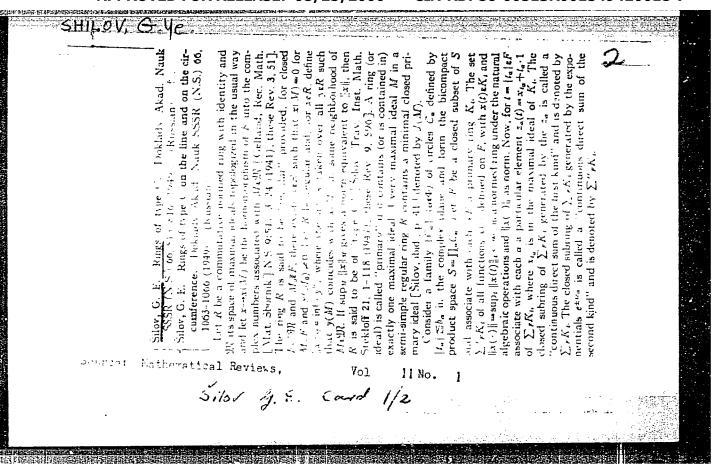
interval and  $C_n$  the class of all functions with n continuous lowing basic result: if the function x in  $D_n$  has the Fourier coefficients  $a_n$ , where  $2\pi a_n = \int_0^{2\pi} x(t)e^{iut}dt$ , then the relation  $\lim_{n\to\infty} \|a_n e^{int}\| = 0$  holds in R. It then follows by a reductio ad absurdum that  $\|e^{tat}\| \le C(|n|^N+1)$  for some N, and hence that the required P exists.

> No. 4 Vol

The Monay and the normed ring consisting of functions

antiques of the constraint and a street theremakter specialities. without any loss of generality to the case a = 0,  $b = 2\pi$ ),  $D_n$  the class of all infinitely differentiable functions on that where  $0 \le \alpha_{n+n} \le \alpha_n \alpha_n$  and  $\lim \alpha_n^{1/n} = 0$ , leading to the fol-

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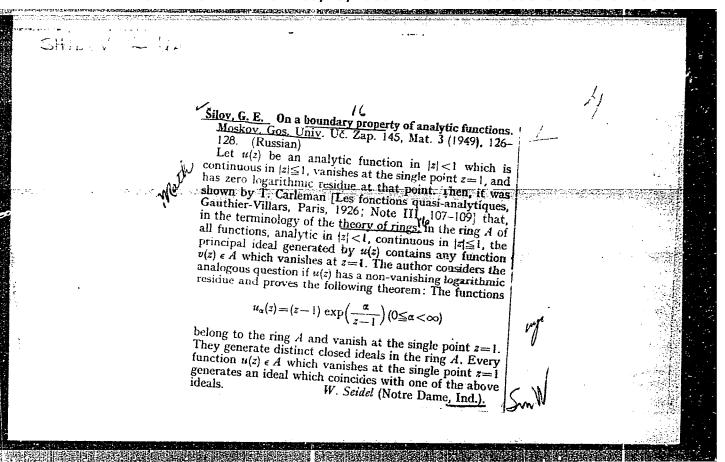


Let X be all altottary ring of type C and denote by  $|z_n|$  a system of generators for R. Define  $C_n$  to be the set of  $I_n$  with  $|I_n| \le \max_X |z_n(M)|$ . Then the space  $\mathfrak{M}_N$  of maximal ideals of R can be considered embedded in  $S = \prod_{n \in \mathbb{Z}_n} R_n / (t)$ . Then  $R = \sum_{n \in \mathbb{Z}_n} R_n / (t)$ . Conversely, if  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Then  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Conversely, if  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Then  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Conversely, if  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Then  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Conversely, if  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Then  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Conversely, if  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Then  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$ . Conversely, if  $R = \sum_{n \in \mathbb{Z}_n} r R_n / (t)$  are also given in the above two situations for regularity and semi-simplicity of the direct sums involved. The second paper is concerned with applications of the above results in the following special cases. (1) The ring R is a "homogeneous ring on a circumference." That is, R is a ring of functions x(t) defined on the closed interval  $[0, 2\pi]$ , with 0 and  $2\pi$  identified, generated by  $e^{\pm it}$  and such that x(t+h)eR,  $\|x(t+h)\| = \|x(t)\|$  for arbitrary real R. In this case all of the primary rings R/L(t) are isomorphic. (2) The ring R is a ring of type C consisting of unctions defined on the closed interval [x, b], possessing one generator and containing all functions with continuous derivatives. A number of other concrete examples are also derivatives. A number of other concrete examples are also

Mathematical Reviews,

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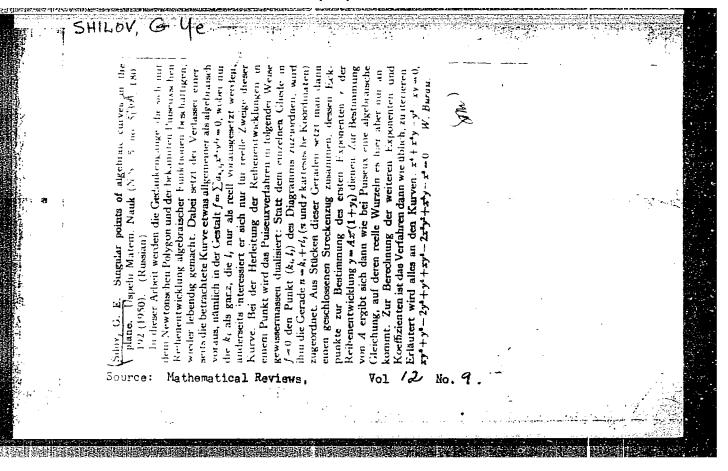
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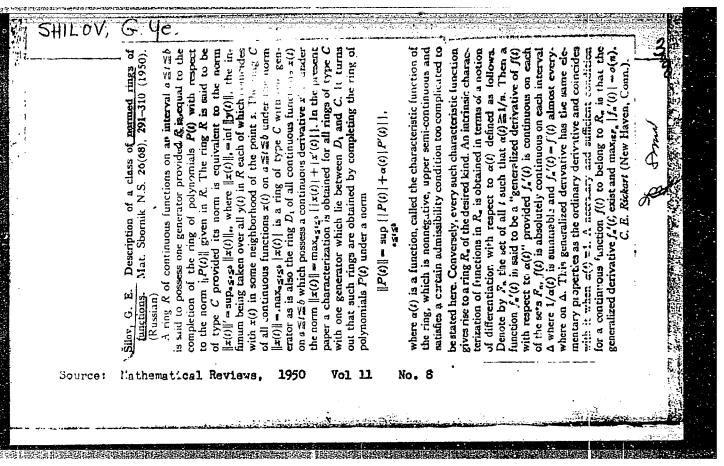
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SILOV, G. E.

Silov, G. E. On rings of functions with uniform convergence. Ukrain. Mat. Zurnal 3, 404-411 (1951). (Russian)

The author first establishes a simple generalization of the complex form of the Stone-Weierstrass theorem [M. H. Stone, Math. Mag. 21, 167–184, 237–254 (1948); these Rev. 10, 255], as follows. Let C(G) be the (complex) Banach algebra of all continuous complex-valued functions on the compact Hausdorff space G, with the usual algebraic operations and norm. Let L be a closed subalgebra of C(G) containing all constants. Let  $\Lambda$  be a closed subalgebra of L

such that  $x \in A$  implies  $\bar{x} \in A$ . The equivalence relation  $\sim$ on G such that  $t_1 \sim t_2$  if and only if  $f(t_1) = f(t_2)$  for all  $f \in A$ obviously dissects G into disjoint closed sets  $\tau$ . For every such  $\tau$ , let  $J(\tau)$  be the ideal in L of all functions in L which vanish on  $\tau$ . There is an obvious and natural isomorphism carrying the difference algebra  $L-J(\tau)$  onto an algebra of functions defined on  $\tau$ . The generalized Stone-Weierstrass theorem asserts that if  $f \in C(G)$  and if f agrees on every  $\tau$ with a function in  $L-J(\tau)$ , then  $f \in L$ . For  $L=\Lambda=C(G)$ , this is exactly the Stone-Weierstrass theorem. The theorem is applied to prove the following result. Let C be the algebra  $C(|z| \le 1)$  and A the closed subalgebra of C consisting of the functions which are analytic on |z| < 1. Let  $\{A, \Sigma\}$  be the smallest closed subalgebra of C containing A and the real functions  $f \in \Sigma$ . A closed subset S of  $|z| \le 1$  is said to be admissible if S has void interior and if for all zo non-e S,  $|z_0| < 1$ , there is a continuous curve running from  $z_0$  to |z|=1 which does not intersect S. Then it is proved that  $\{A, \Sigma\} = C$  if and only if all sets of points equivalent under the set of functions  $\Sigma$  are admissible. This generalizes a theorem attributed to Hurgin [Moskov. Gos. Univ. Učenye Zapiski 145, Ser. Mat. 3 (1949) (unavailable)].

E. Hewitt (Seattle, Wash.).

50' MATH REVINOLIH, NO.9, OCT. 1953

PP. RZI-9Z4 - UNCLASSIFIED

USSR/Mathematics - Functions "Homogeneous Rings of Functions," G. Ye Shilov "Uspekhi Matemat Mauk" Vol VI, No 1 (41), pp 91-137 Describes one important class of normed rings of functions; rings of functions given in bicompact group and invariant relative to displacements with respect to this group. Main results of this study are constr of continuous direct sum of primary rings in bicompact commutative group and proof of possi- bility of obtaining by this means any homogeneous  LC  17753 USSR/Mathematics - Functions (Contd) Jan/Feb 51 ring of functions; Fourier scries relative to continuous characters; regular normed rings; con- tinuous sums of primary rings; homogeneous rings of functions; certain application, and examples. 32 ref.  17753

SHILOV, G. Ye.

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USSR/Mathematics - Vectors

Sep/Oct 51

"Vector Smooth Functions," G. Ye. Shilov

"Uspekh Matemat Nauk" Vol VI, No 5 (45), pp 176-184

Considers continuous complex-valued functions w(x,y) = u(x,y)+iv(x,y) defined in a certain region G of the plane of real variables x and y. Each such function w can be interpreted as a vector field  $\overline{w} = (u,v)$  defined in G. And conversely, each vector field  $\overline{w} = (u(x,y), v(x,y))$  defined in G can be written in the form of a complex function w = u+v. Notes certain properties of divergence and curl functions.

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